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BATTERY SEPARATORS BASED ON POLYPHENYLQUINOXALINE POLYMER BLEND--ETC(U)
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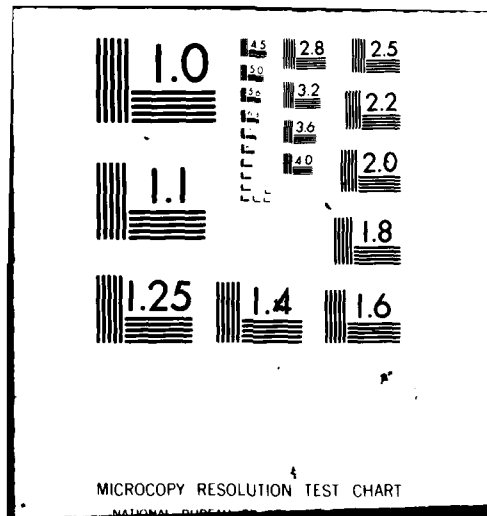
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BATTERY SEPARATORS BASED ON POLYPHENYLQUINOXALINE POLYMER BLENDS

BY ISAAC ANGRES, LEN KOWALCHIK,
WENDY PARKHURST

RESEARCH AND TECHNOLOGY DEPARTMENT

1 APRIL 1981

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alkaline battery separators; however, because of cost considerations, it is not competitive with similar state-of-the-art materials.

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FOREWORD

This document is the final report on battery separators based on polyphenylquinoxaline (PPQ) polymer blends. The report describes in detail the technical development of a new separator material intended for use in secondary batteries with alkaline electrolytes. Included are summaries of the data obtained to identify and characterize these new materials and comparison data for currently available separator materials. Funding for this work was provided by NAVSEASYS COM, Task Number 62543N/SF43431302/1R33JE701.

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INTRODUCTION

The purpose of this program was to develop preparative methods, quality control parameters, and processes expressly directed toward the efficient generation of reliable polyphenylquinoxaline based film for high-performance alkaline type batteries.

To accomplish the above, the program was divided into three separate tasks.

TASK NUMBER ONE: Development of a porous separator by means of leachable or hydrophilic additives, and compatibilization of the polyphenylquinoxaline in suitable solvents.

TASK NUMBER TWO: Quality assurance testing. The scope of this task was to establish and/or select tests to control raw material variability, in-process parameters, and final product quality. The following characteristics of the membrane were to be evaluated in selection of tests for quality control of the final product:

- a. AC resistance
- b. Zinc penetration
- c. Hydroxyl, silver and zinc diffusion
- d. Dimensional stability
- e. Chemical stability

TASK NUMBER THREE: Cycle Testing. This task required construction of suitable cells and controls with cellophane to assess any improvement over the state-of-the-art technology.

PREPARATIVE METHODS AND COMPATIBILIZATION

The earlier investigations¹ of the development of polymeric membranes based on polyphenylquinoxalines (PPQ) had as the leachable additive polyvinylpyrrolidone and m-cresol as the solvent. However, the use of m-cresol as the solvent was somewhat cumbersome because of its high boiling point. In addition, when the need arose to use other leachable additives, we encountered a problem of polymer-polymer compatibilization when m-cresol was used as the solvent.

It is known that the unique characteristics of homopolymers and copolymers are conferred by their specific chemical and stereo-structures, by their molecular weight distribution, and by their intra- and inter-chain interactions. Although such homogeneous materials have numerous useful chemical and physical properties, it is often desirable to seek improvements (i.e., lower their inherent electrical resistance) in their characteristics or processing requirements. In order to accomplish the above improvements one finds that it is necessary to prepare multicomponent polymer systems. Thus, homogeneous blends (in solution), comprising mixtures of polymers, provide a route toward combinations of properties not otherwise available.

In this study our efforts focused on the preparation of homogeneous polymer blends in chloroform. The above blends contain PPQ as the main polymer and other resins such as polyvinylacetate, polyvinylpyrrolidone, vinylacetate/vinylpyrrolidone copolymer, cellulose acetate, cellulose triacetate, and polybrene (a diquatarnary ammonium bromide polymer). The use of chloroform as the solvent solves the problem of PPQ compatibilization with other polymers in m-cresol. Similarly, it will be noted that preparation of the membranes is faster because of the ease of evaporation of the chloroform.

EXPERIMENTAL.

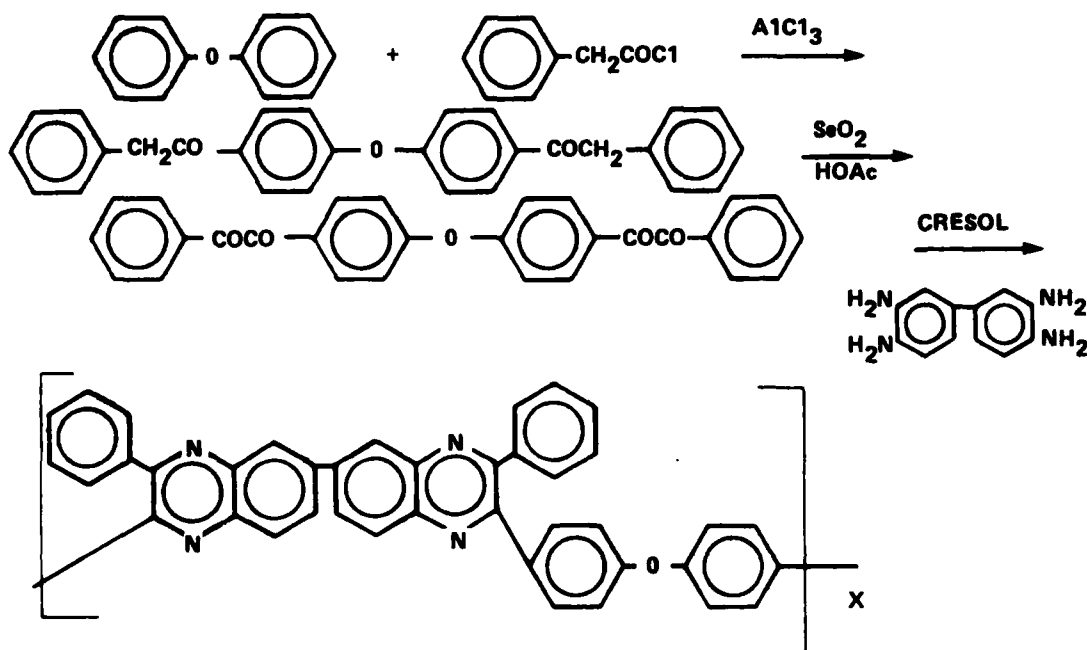
Polymer Preparation.

Poly-2,2'-(p,p'-oxydiphenylene)-6,6'-Di(3-phenylquinoxaline)

The PPQ based polymer used in the preparation of the membranes for this study was purchased as a 10% solution in m-cresol from the Narmco Division of the Whittaker Corporation. The synthetic route to prepare this polymer is as follows:

¹Kilroy, W. P. and Duffy, J. V., "Development of an Improved Separator Material for Alkaline-Silver Zinc Batteries," NSWC TR 76-135, Feb 1977.

The reported inherent viscosity for this polymer is 2.05 dl/g and the glass transition temperature is 693°K (420°C)². Polyvinylacetate (low, medium, and high molecular weight), polyvinylacetate/vinylpyrrolidone copolymer, polybrene, polyvinylpyrrolidone, cellulose acetate, and cellulose triacetate were all obtained from Aldrich Chemical Company.



Membrane Preparation.

The following procedure applies to all of the above polymers when blended with the PPQ and using chloroform as the solvent:

Thirty grams of the 10% PPQ solution was added to a suitable container followed by 2 g of any of the above polymers or 2 g of a mixture of the above polymers. To the above mixture 100 ml of chloroform was added and the resulting composition was stirred thoroughly until a homogeneous solution was obtained. The homogeneous solution was used for casting purposes.

The membranes were prepared by spreading the homogeneous solution onto a glass plate (16 cm x 28 cm x 0.9 cm) with a metal bar. The thickness of the final film was controlled by means of masking tape which was placed along the edges of the glass plate (three layers of tape \approx 1 mil thickness). It was necessary to thoroughly wash the glass plate with water and detergent and then to rinse with isopropyl alcohol to insure good wetting by the polymer solution.

²Hergenrothen, P. M., and Levine, H. H., "Phenyl-Substituted Polyquinoxalines," J. Polymer Sci., Part A-1, 5, 1967, pp. 1341-57.

Following the casting of the film, the solvent (chloroform) was allowed to evaporate slowly for 2-3 minutes, or until cloudiness appeared, by partially enclosing the plate in a plastic container, and then immersing the plate in a 50:50 methanol-water bath, and allowing to stand for 10 minutes. The film was washed with water and dried in air. Films obtained by this method had good handleability and did not shrink on drying.

The leachable additives were either extracted with water or hydrolyzed in KOH (45%) at 80°C to create porosity.

DISCUSSION.

Incompatibility (insolubility) is an often encountered problem that prevents the preparation of useful blends. The use of chloroform as the solvent allows for the preparation of many useful PPQ polyblends in solution. Evidently chloroform acts as a good compatibilizing agent because it forms weak hydrogen bonds with the PPQ, as shown in Figure 1. By tying up all of the PPQ with hydrogen bonding one can then dissolve other polymers in the same system without encountering the problem of PPQ precipitation.

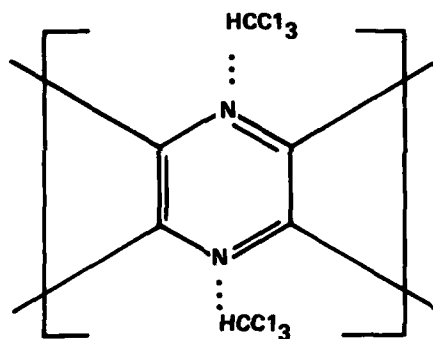


FIGURE 1 HYDROGEN BONDING OF CHLOROFORM WITH PPQ

The use of chloroform also allows one to make all the possible mathematical combinations of mixtures all of the above blends (i.e., one could make a blend of PPQ/cellulose acetate/and polyvinylpyrrolidone, etc.).

QUALITY ASSURANCE TESTING

The use of quality assurance testing is of extreme importance, as it tells one whether or not the desirable characteristics of a new separator have been obtained. The following characteristics were measured:

- o AC resistance,
- o Zinc penetration,
- o Hydroxyl, silver and zinc diffusion,
- o Dimensional stability, and
- o Chemical stability.

a. AC RESISTANCE.

The electrical resistance of a separator is one of its most important properties because it is a valuable indicator of the performance of the separator in working cells. The electrical resistance was measured by the alternating current method as described in Reference 3.

Using the AC method, electrical resistance of membranes based on PPQ blends were measured in 45% KOH at room temperature using a plexiglass cell as shown in Figure 2. The circuitry used for the resistance measurement has been described by Kilroy and Moynihan⁴. The separator resistance was obtained as the difference between the cell resistance with and without the separator, in $m\Omega/in^2$ and then converted to $\Omega\text{-cm}$. The results of resistance measurements for different PPQ/blends are summarized in Table 1.

The results in Table 1 indicated that the blend most useful as a battery separator was PPQ/CA (60/40). It was also observed that it took about nine times longer for PPQ/CA (60/40) to achieve constant resistance when compared to cellophane as shown in Figure 3.⁵ This was in agreement with the fact that the PPQ/CA matrix was not as hydrophilic as cellophane.

³Cooper, J. E. and Fleisher, A., "Characteristics of Separators for Alkaline Silver Oxide Zinc Secondary Batteries," AD-447301, AF Aero Propulsion Lab, Wright-Patterson AFB, Ohio, 1964, p. 69.

⁴Kilroy, W. P. and Moynihan, C. T., "Measurement of Battery Separator Resistances in Low Impedance Conductivity Cells by A-C Bridge Techniques," J. Electrochem Soc., Vol. 125, 1978, p. 520.

⁵Angres, I., Duffy, J. V., and Kilroy, W. P., "New Heat and Chemically Resistant Polymeric Membranes," in Proceedings--Twenty-Eighth Power Sources Symposium, 15 June 1978.

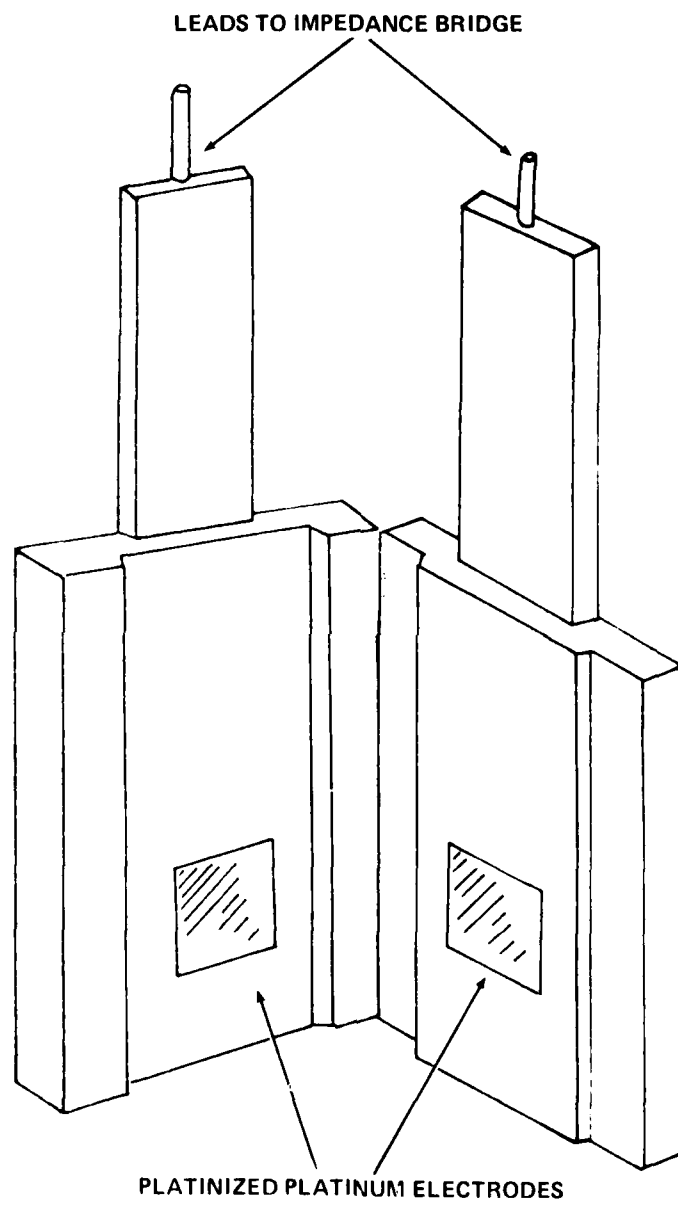


FIGURE 2 RESISTANCE CELL

TABLE 1 RESISTANCE OF PPQ COMPOSITE MEMBRANES

MEMBRANE ^a	RESISTANCE IN 45% KOH ohm-cm	FILM THICKNESS MILS	
		DRY	IN 45% KOH
PPQ/CA	40	1.3	2.1
	55	1.8	2.8
	60	1.7	2.9
PPQ/CT	100	2.2	3.5
	150	2.8	4.0
	125	2.1	3.3
PPQ/PVA	200	1.1	2.1
	230	1.4	1.9
	280	1.8	2.7
PPQ/PVP	1000	1.0	1.4
	1000	0.7	1.0
	1000	0.4	0.6

^aThe ratio of PPQ/X-Polymer is 60/40.

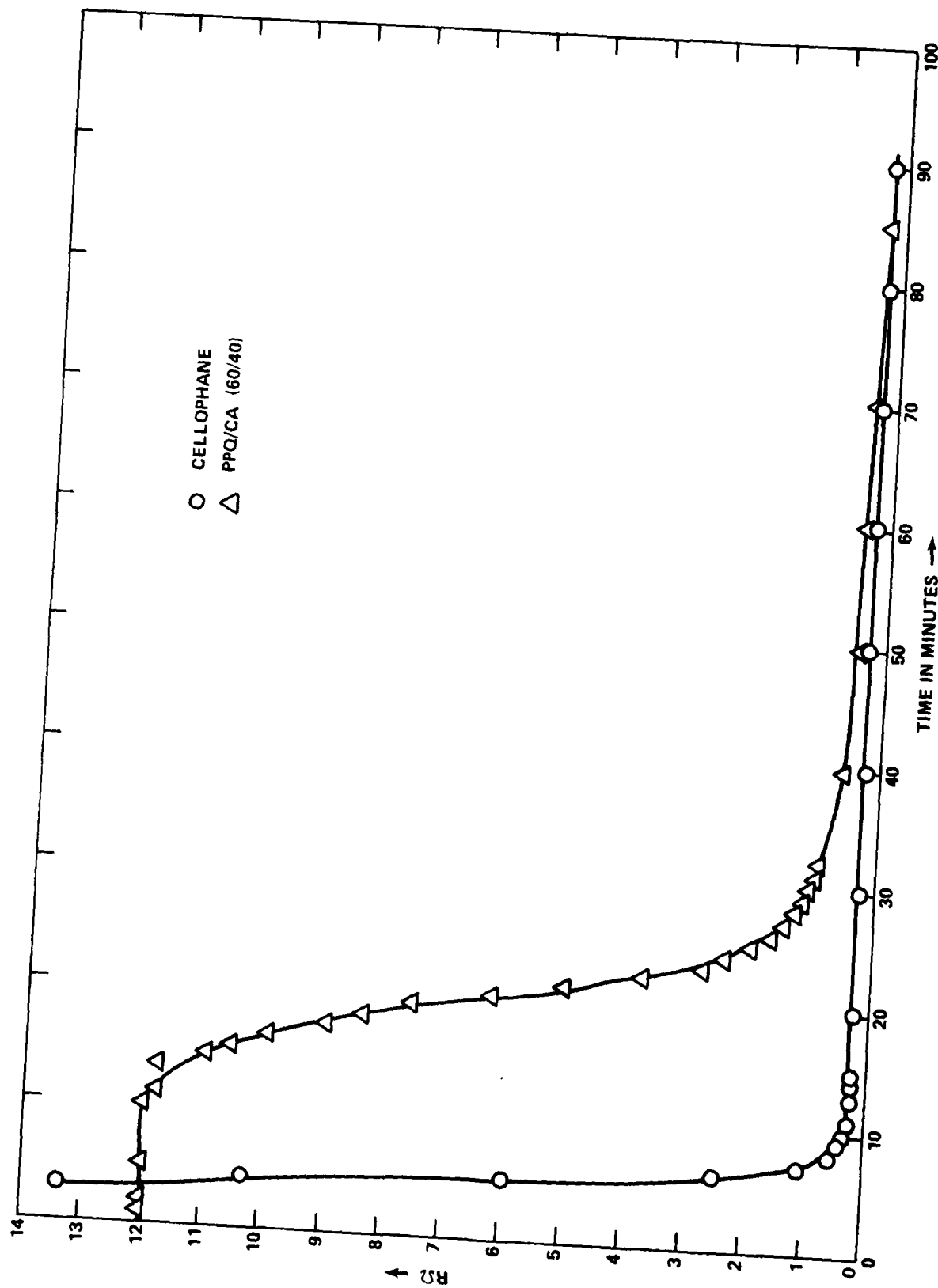


FIGURE 3 COMPARATIVE RATES OF ACHIEVING CONSTANT RESISTANCE

b. ZINC PENETRATION.

The main purpose of the zinc penetration test was to establish a reliable and meaningful quantitative measurement of the rate at which zinc dendrites penetrate alkaline zinc separators under controlled conditions.

The zinc penetration cell design is illustrated in Figure 4. The cathode was a Pellon clad zinc sheet. The anode was a partially charged nickel hydroxide ($\text{Ni}(\text{OH})_2$) electrode clad with one or more layers of the test separator material. The approach was to determine the time required for zinc dendrites to form and penetrate the test separator causing a short circuit.

The following test conditions were selected to render the zinc penetration test as reproducible and simple as possible.

1. State of charge of the $\text{Ni}(\text{OH})_2$ reference electrode - 0.0005 Ah
2. Working current density - 100mA/inch²
3. Electrolyte - 42% KOH saturated with zincate
4. Soak time - overnight for single layered, and 2-3 days for multi-layered separators.

The results of the zinc penetration studies on PPQ/CA (60/40) compared to other separators are given in Table 2.

The results in Table 2 indicate some sample variability. Because the sample does not swell when wet, it is advisable to analyze this data with caution. The data indicates silver-cellophane to be the best dendrite stopper.

c. HYDROXYL, SILVER AND ZINC DIFFUSION.

The diffusion of hydroxyl, zinc, and silver ions through the separator is an important characteristic of the separator. Each type of separator has its own characteristic diffusion properties. The diffusion properties, characterized by the flux of species through the membrane, have been well established for cellulosic separators. The procedure and theory for determination of diffusion properties of PPQ/CA (60/40) was taken from Reference 3.

1. Hydroxyl Diffusion. The diffusion of OH^- ions through PPQ/CA (60/40) was studied by following the pH change across the separator. The flux of OH^- ions was calculated according to the expression³:

$$\text{FLUX} = \frac{\Delta M}{A \Delta t} = \frac{\Delta C}{\Delta t} \times \frac{V}{A} \quad (\text{Moles/Unit Time-Unit Area})$$

The results of the hydroxyl diffusion studies across PPQ/CA (60/40) compared to state-of-the-art materials are represented in Figure 5.⁵ The results indicate that hydroxyl ion diffusion is faster through cellophane than through PPQ/CA (60/40). The average flux of OH^- ions through cellophane was 1.61×10^{-3} mole/min-square inch whereas the flux for PPQ/CA (60/40) was 1.06×10^{-3} mole/min-square inch. The differences in flux occur because at the molecular

³See footnote 3 on page 11.

⁵See footnote 5 on page 11.

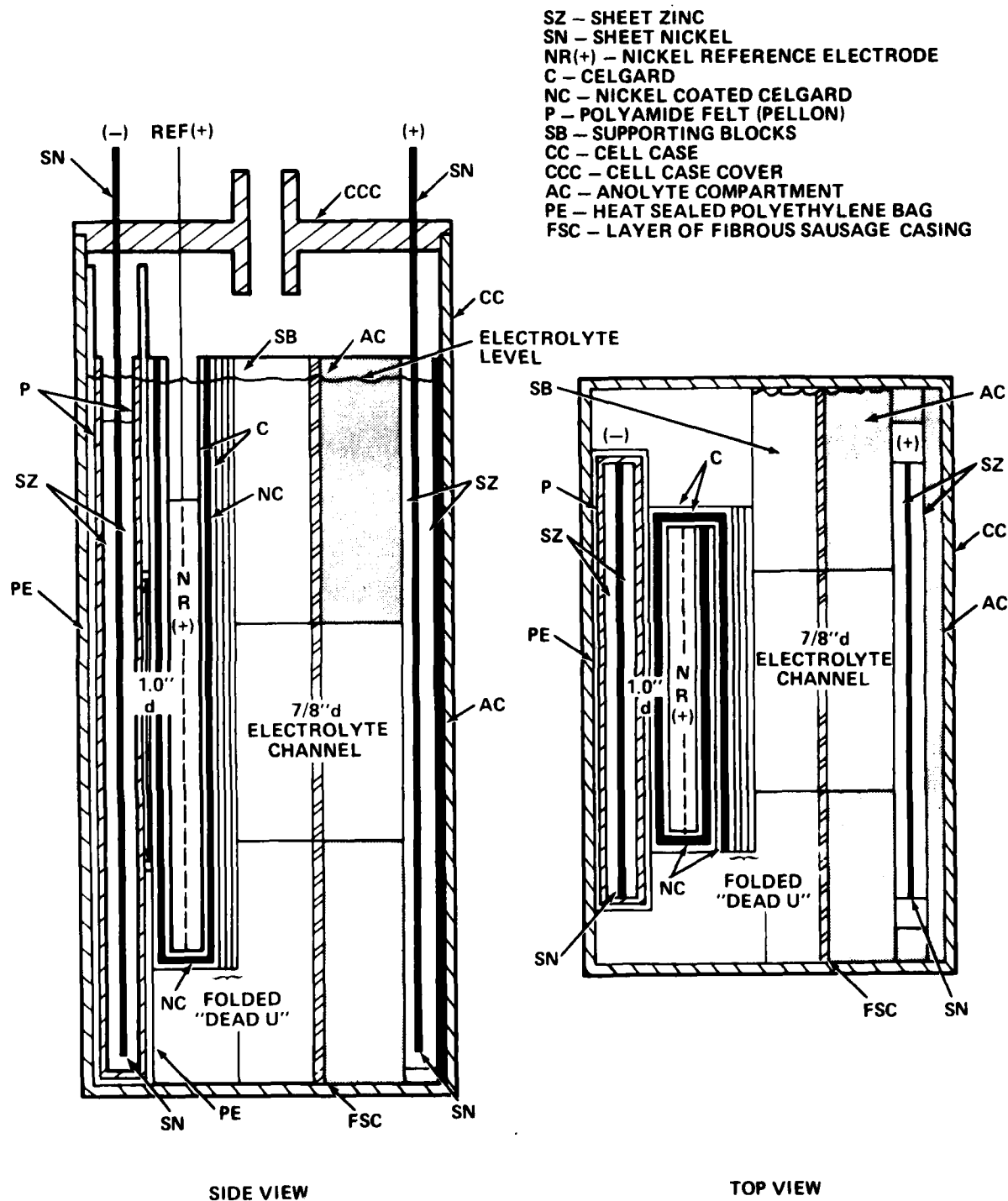


FIGURE 4 ZINC PENETRATION CELL DESIGN

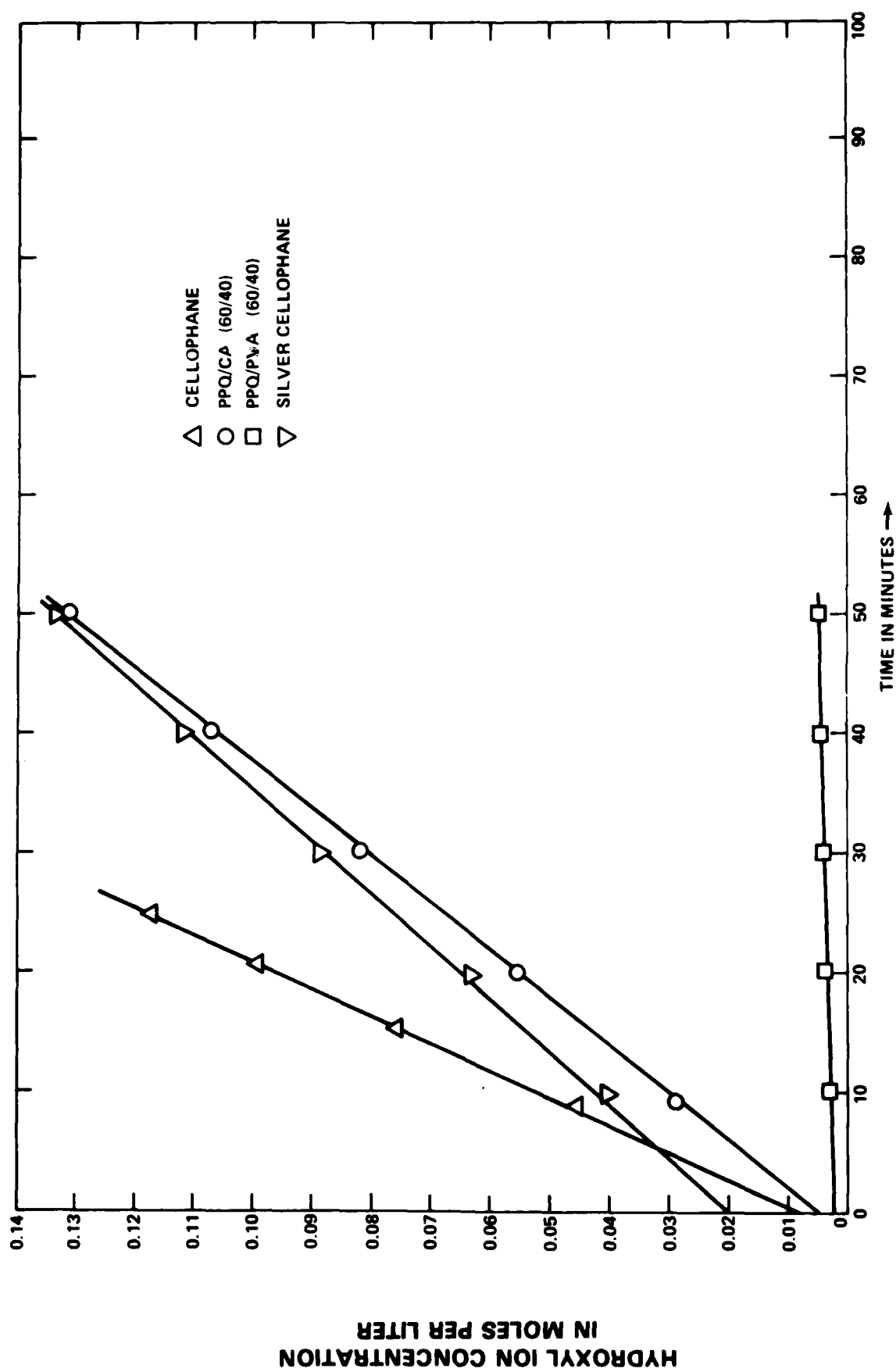
TABLE 2 ZINC PENETRATION RESULTS ON PPQ/CA MEMBRANES

Sample #	Hours to Short	Thickness (mils)	hrs/mil	Resistivity $m\Omega\text{-inch}^2$	$\frac{m\Omega\text{-inch}^2}{\text{mil}}$
a					
PPQ/CA 27	1.28	1.0	1.28	20	20
PPQ/CA 28	0.68	1.0	0.68	17	17
PPQ/CA 29	1.00	1.0	1.00	18	18
PPQ/CA 30	1.45	1.0	1.45	17	17
b					
C-19-1	7.45	3.0	2.48	14	4.7
C-19-2	6.10	3.0	2.03	13	4.3
c					
FSC-1	12.1	7.5	1.62	38	5.0
FSC-2	13.2	7.5	1.76	38	5.0
FSC-3	13.9	7.5	1.85	38	5.0

^aPPQ/CA (60% PPQ and 40% cellulose acetate)

^bCellophane treated with silver. (YEC treatment)

^cFSC = Fibrous sausage casing.

FIGURE 5 DIFFUSION OF OH⁻ THROUGH SEVERAL MEMBRANES

level, cellophane comes close to being a heterogeneous molecular sieve⁶, and its intra-molecular hydrogen-bond interactions allow wettability and diffusion to occur somewhat faster. The lower flux of PPQ/CA (60/40) can be explained by the non-polar and hydrophobic nature of the PPQ. Similarly, it is noted that cellulose acetate provides wettability and electrolyte flow in PPQ/CA (60/40).

2. Silver Diffusion. The flux of silver was measured using a radioactive tracer technique using ¹¹⁰Ag. The measurement was done on PPQ/CA (60/40) and cellophane.

Four 15 mg aliquots of Ag₂O were irradiated using a reactor for 12 hours, each aliquot yielding a net activity of about 20 Ci of ¹¹⁰Ag. The radioactive Ag₂O was dissolved in 40% KOH by stirring overnight. The solution was filtered to remove any undissolved Ag₂O and the filtrate made up to 250 ml. This solution was then transferred to one of the compartments of the diffusion chamber and an equal volume of 40% KOH (without ¹¹⁰Ag) was transferred to the other (empty) compartment. Both compartments were magnetically stirred during the entire diffusion period. Aliquots of 1.0 ml were removed at intervals of 0, 2, 6, 8, 24, 48, 96 and 168 hours after initiation of the diffusion period. The initial silver concentration in the compartment containing ¹¹⁰Ag was determined by comparison with a silver standard which was irradiated simultaneously with the Ag₂O. The aliquots from both compartments were counted on a NaI(Tl) wire type detector for periods of up to 10,000 seconds.

PPQ/CA (60/40) allowed ZERO diffusion of the silver over the course of one week at a silver concentration of $1.1 \times 10^{-5}M$. (This sample was also allowed to diffuse for up to 19 days with no measurable diffusion after that period.) Approximately 0.27% of the total amount of silver initially present was retained by the membrane.

On the other hand, cellophane allowed significant diffusion during a period of four to twenty four hours. The silver concentration decreased from $1.1 \times 10^{-5}M$ to $0.67 \times 10^{-5}M$ after four hours, with a concentration of $0.45 \times 10^{-5}M$ after 24 hours. The compartment with no initial silver showed an increase in the silver concentration to $0.54 \times 10^{-5}M$ after 24 hours, yielding a retention for cellophane of approximately 10% of the initial amount of silver present in the diffusion chamber.

In summary, the silver diffusion experiments indicate that PPQ/CA (60/40) did not allow permeation of silver species, while cellophane is highly permeable to silver.

3. Zinc Diffusion.

This method consists of placing a membrane between two half cells with one side having a zinc rich solution and the other having a zinc poor solution. The concentration change is sensed using an amalgamated zinc electrode with Hg/HgO as the reference electrode. For every 10-fold change in the concentration of

⁶Daniels, F. K., "Dialysis," in Kirk-Othmen, Editor, "Encyclopedia of Chemical Technology," (New York: Interscience N.Y., 1950).

the zincate ion, there is a change of 0.0295 volt in the potential of the zinc-zincate ion couple. The calibration curve between zincate concentration and zinc potential in 45% KOH is shown in Figure 6.

The results are summarized in Table 3 and Figure 7⁷ and are compared to standard commercial samples. The experimental data indicates that zinc diffuses faster through cellophane and sausage casing than through PPQ/CA (60/40). The flux value for PPQ/CA (60/40) is one order of magnitude less than that of cellulosic separators, making PPQ/CA (60/40) the better zinc diffusion retardant. This was unexpected because the pore diameters of cellulosic materials are on the order of 20-30 Å, while they are on the order of 2300 Å for PPQ/CA. Therefore it appears that the PPQ/CA (60/40) membrane has a higher tortuosity than cellulosic membranes.

d. DIMENSIONAL STABILITY.

Measurements were taken to evaluate possible dimensional changes in the separator when wetted with KOH electrolyte. Rectangular pieces (approximately 50 x 60 mm) of membrane were cut and accurately weighed after equilibration at ambient laboratory conditions. Samples were then accurately measured with calipers and a micrometer to determine the true dimensions. The specimens were then placed in vials which contained 45% by weight of KOH and studied at 25°C or 80°C. The specimens were removed from the alkali solution at regular intervals and, after blotting the excess solution, were again accurately measured and weighed. The results were recorded over a period of 28 days and are reported as percent change.

The dimensional changes were compared with cellophane. The results are illustrated in Figures 8, 9, and 10.⁵ As expected, the hydrophilic cellophane has absorbed KOH electrolyte to more than double its thickness. Similarly, this is observed in the weight changes of cellophane. The large percentage weight increase in cellophane over that of PPQ or PPQ/CA (60/40) is in agreement with its hydrophilic nature and the dimensional change in its thickness.

e. CHEMICAL STABILITY.

The chemical stability of PPQ/CA (60/40) in 45% KOH saturated with Ag₂O was evaluated at 80°C in a qualitative fashion. The results indicate that PPQ/CA (60/40) is stable under the above environment for periods greater than one year. Therefore, its stability in Ag₂O-Zn cells will be excellent.

⁷Kilroy, W. P., and Laughlin, L., "Diffusion Studies on a PPQ-CA Membrane--A Comparison with Standard Membrane Materials," NSWC/WOL TR 78-174, Dec. 1978.

⁵See footnote 5 on page 11.

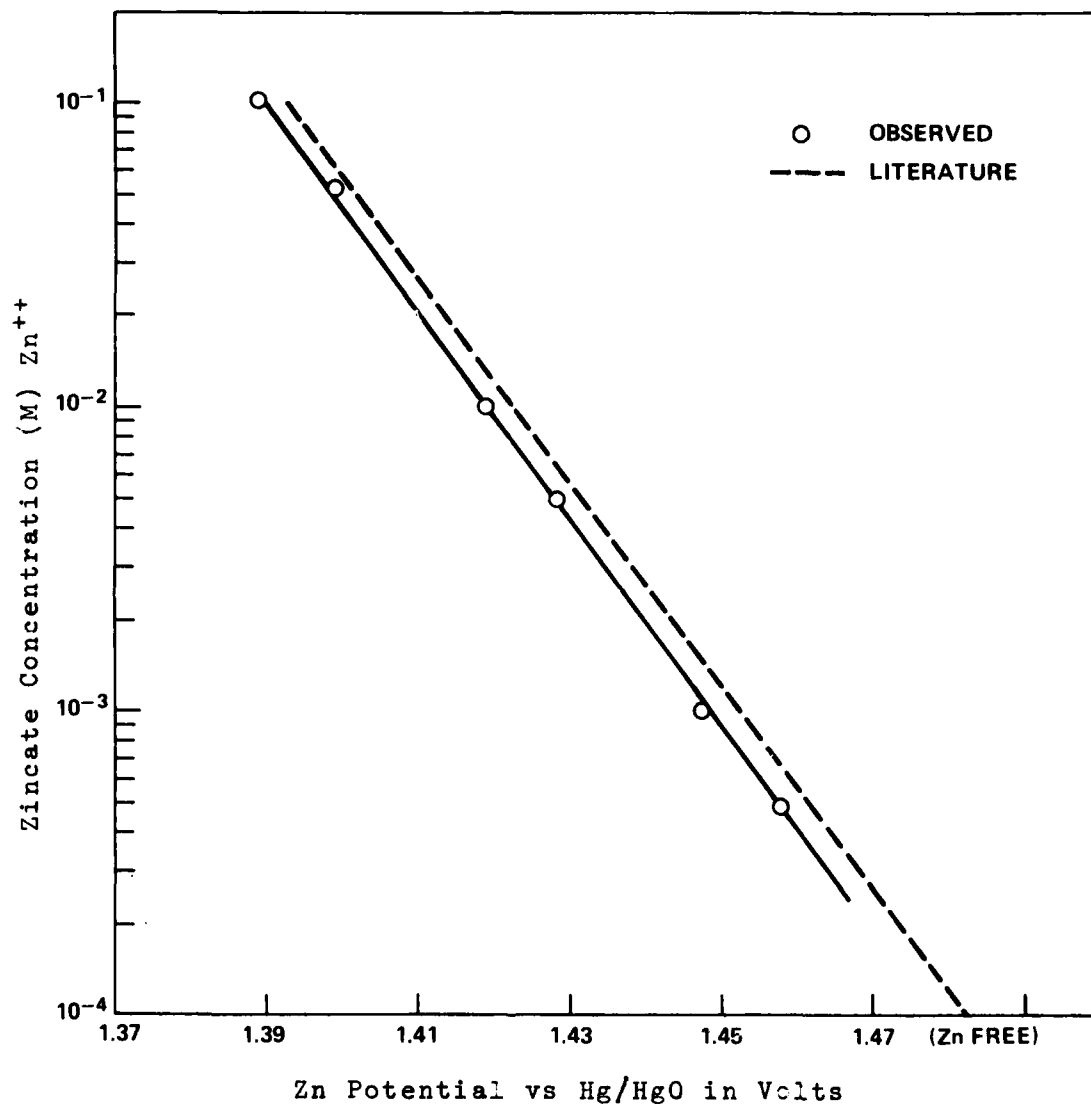


FIGURE 6 CALIBRATION CURVE FOR Zn CONCENTRATION AND POTENTIAL IN 45% KOH

TABLE 3 ZINC DIFFUSION FLUXES USING POTENTIOMETRIC METHODS

Membranes	Sample	V_i	V_f	C_i	C_f	$K \text{ mole/in}^2\text{-min}$
PPQ/CA 60/40	32	1.445	1.439	0.0012	0.0020	7.9×10^{-7}
PPQ/CA 60/40	48	1.437	1.434	0.0023	0.0030	7.2×10^{-7}
PPQ/CA 60/40	63	1.442	1.437	0.0016	0.0023	7.7×10^{-7}
Sausage Casing	1	1.447	1.438	0.0010	0.0021	1.2×10^{-6}
Sausage Casing	2	1.447	1.430	0.0010	0.0035	2.10×10^{-6}
Cellophane	3	1.456	1.429	0.0005	0.0045	2.81×10^{-6}
Cellophane	4	1.464	1.428	0.0003	0.0048	2.73×10^{-6}

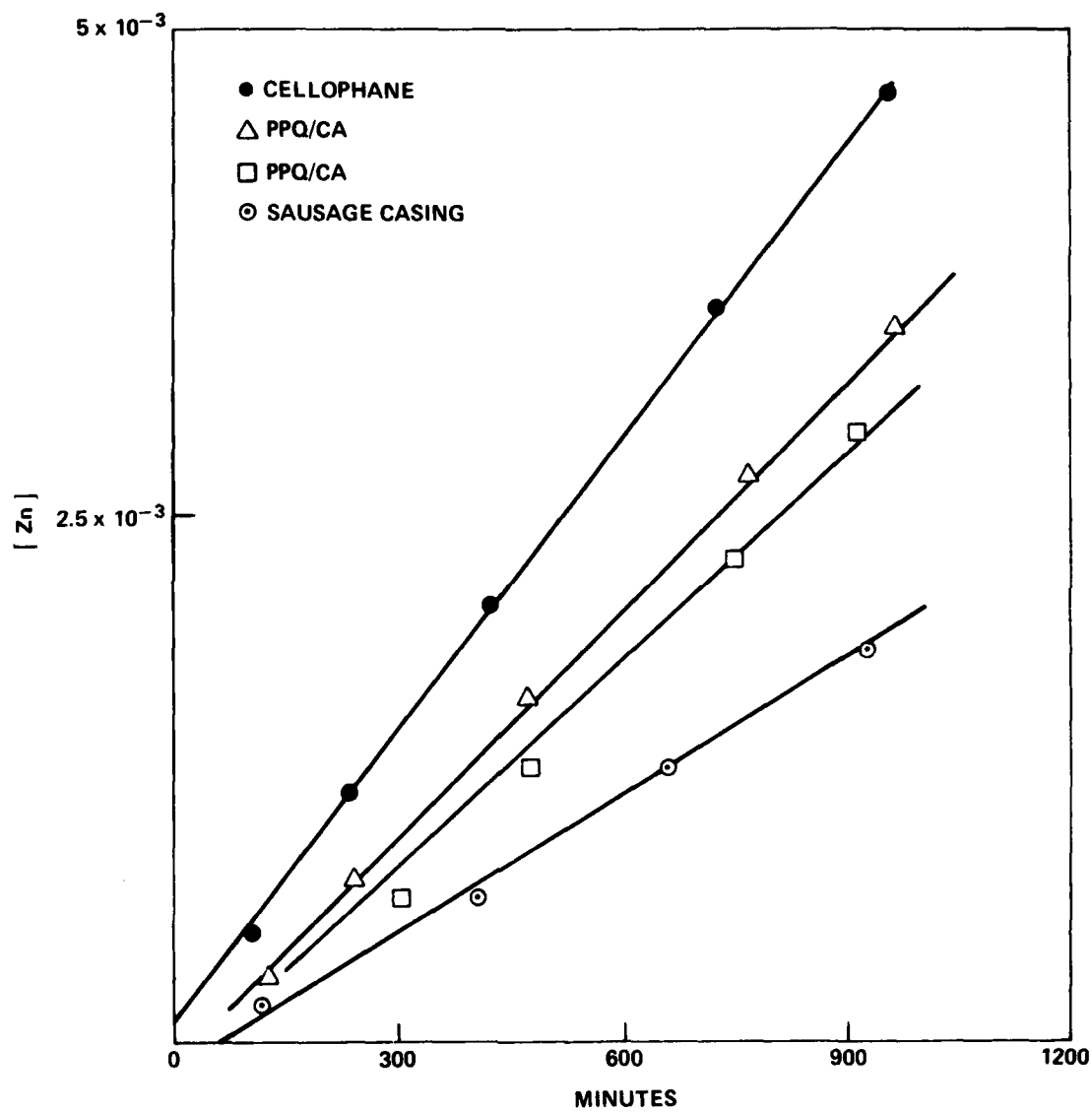


FIGURE 7 DIFFUSION OF Zn USING POTENTIOMETRIC TECHNIQUE

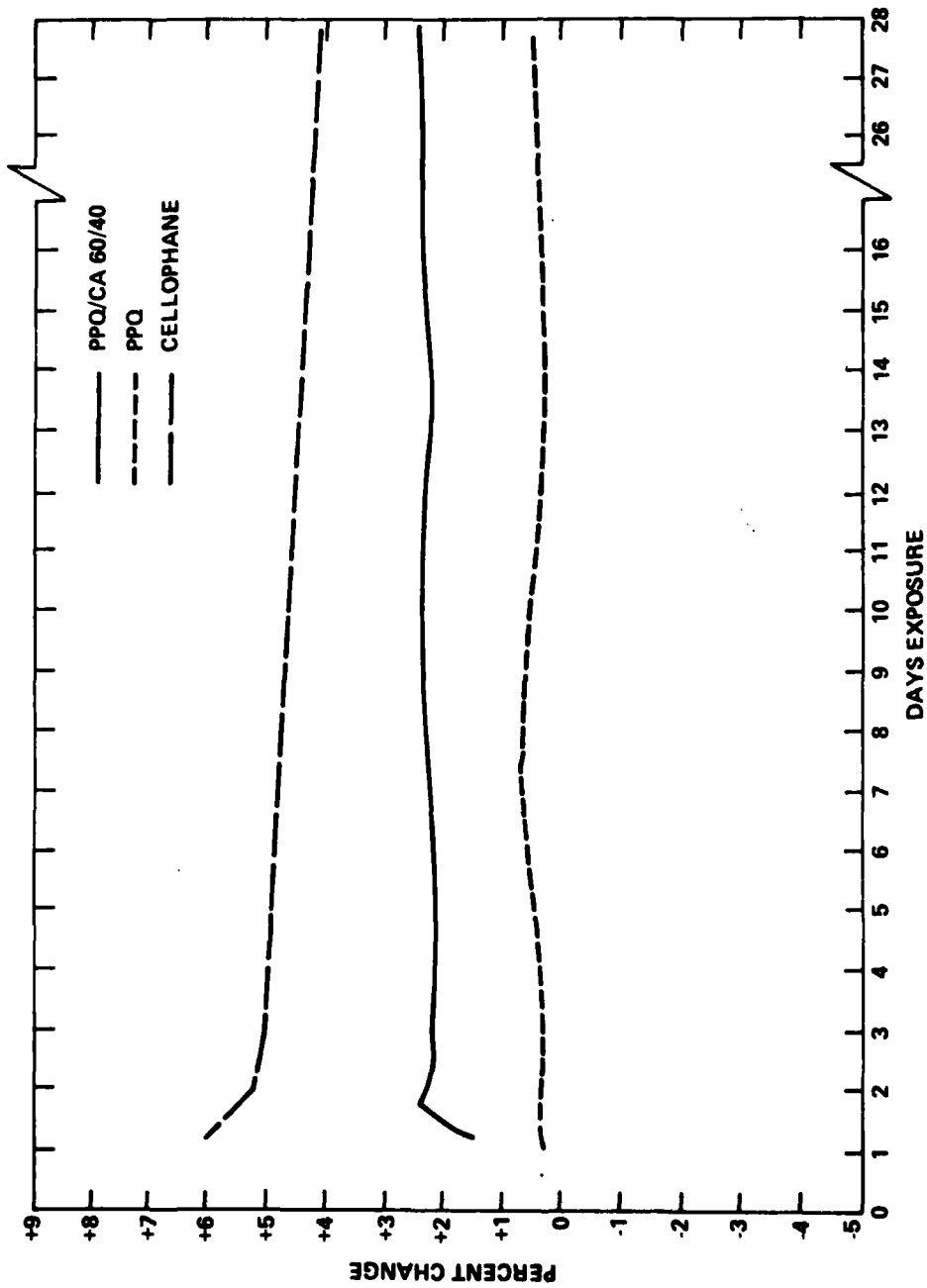


FIGURE 8 DIMENSIONAL CHANGE (L x W) VS EXPOSURE TIME IN 45% KOH AT 25°C

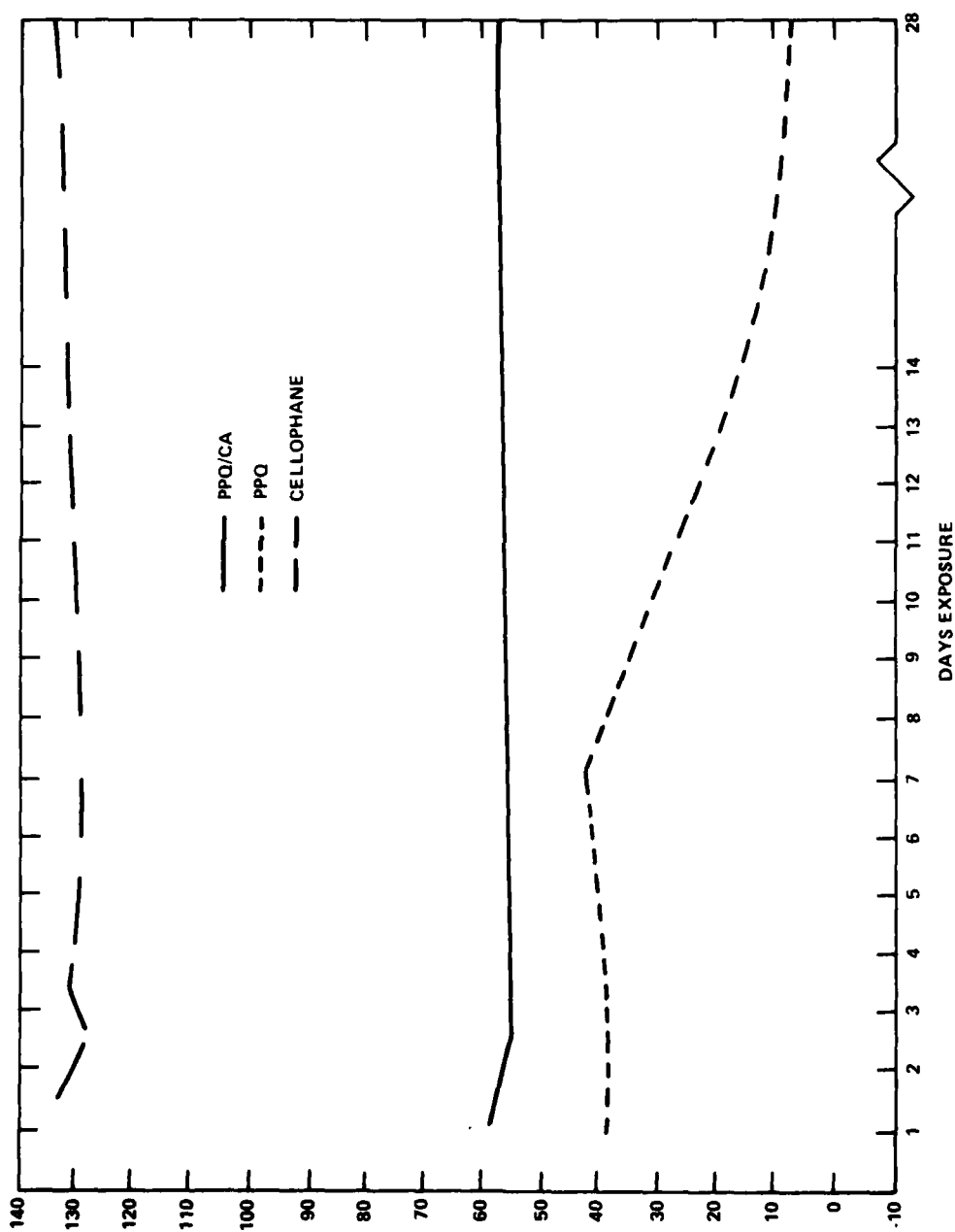


FIGURE 9 DIMENSIONAL CHANGE (THICKNESS) VS EXPOSURE TIME IN 45% - KOH AT 25°C

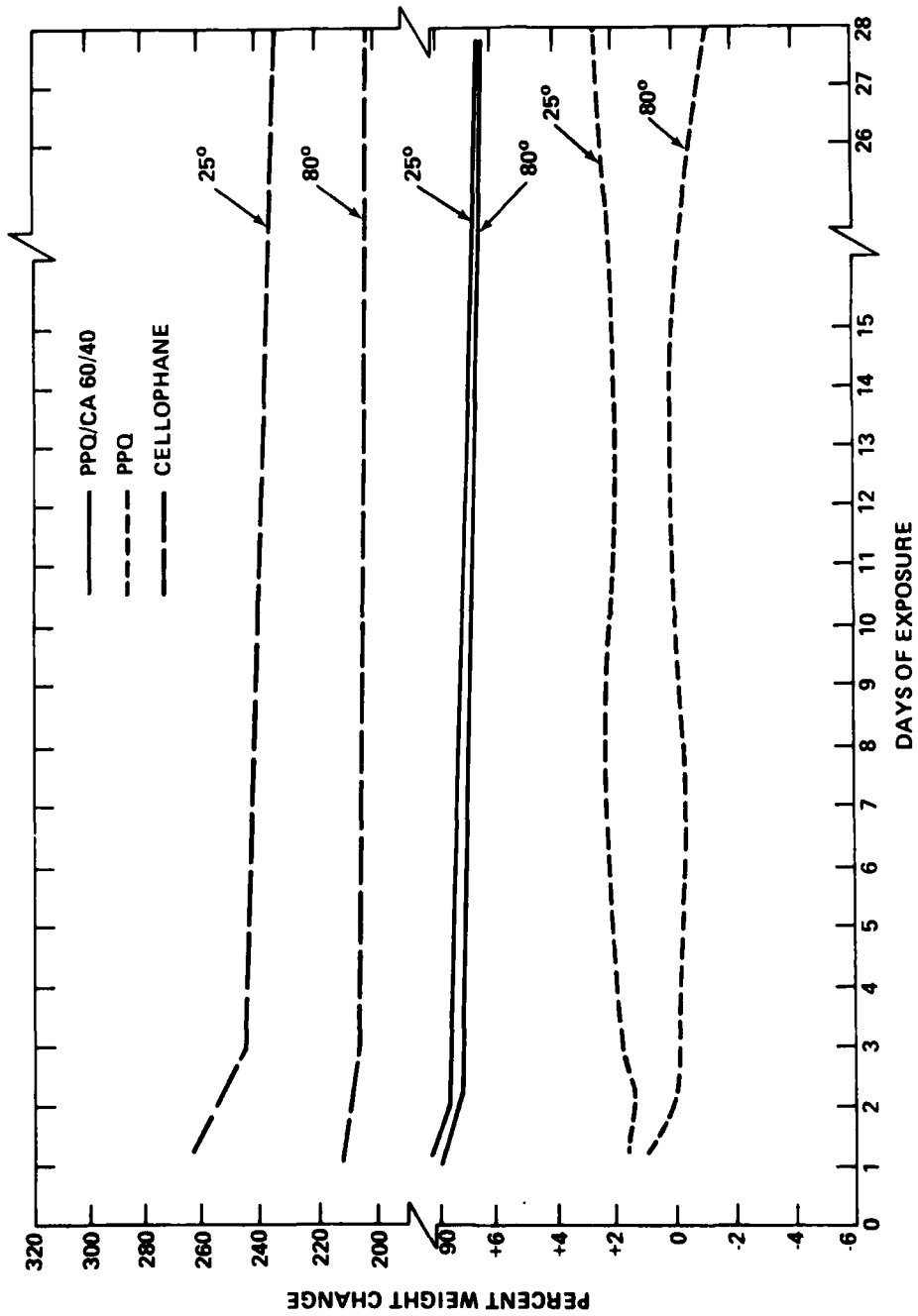


FIGURE 10 WEIGHT CHANGE VS EXPOSURE TIME IN 45% KOH AT 25° AND 80° C

CYCLE TESTING

The ultimate test for a separator is in cycle life testing. If a battery separator is to be considered satisfactory, it must have a long cycle life. The cells used for cycle life testing consisted of five plates, usually two silver oxide plates wrapped in the U configuration and three zinc plates. The experimental plan was to test five layers of test material, ie., PPQ/CA (60/40) and compare it with five layers of cellophane. Six cells of each group were to be continuously cycled at constant current to short circuit failure at a temperature of 25°C. The two positive plates were wrapped with one layer of pellen and five layers of test material or cellophane, and were assembled in the U-configuration. The cells had a nominal capacity of 3 Ah and the depth of discharge (DOD) was 100%. The cells were discharged at a constant current of 1 amp, and then charged at 0.4 amp for the first 60% of capacity, followed by 0.25 amp until the voltage reached 2.05 V.

The results of cycling characteristics are summarized in Figure 11. The data points are the average of six groups of cells both for the PPQ/CA (60/40) and the cellophane. Figure 11 indicates that in both the PPQ/CA (60/40) and the cellophane, there is a loss in capacity which is dependent on cycling. At about cycle number 32 the cellophane shows a sharp decline in capacity, while the PPQ/CA (60/40) continues to deliver approximately 1Ah up to at least cycle number 49. In both cases the mode of failure was short circuit.

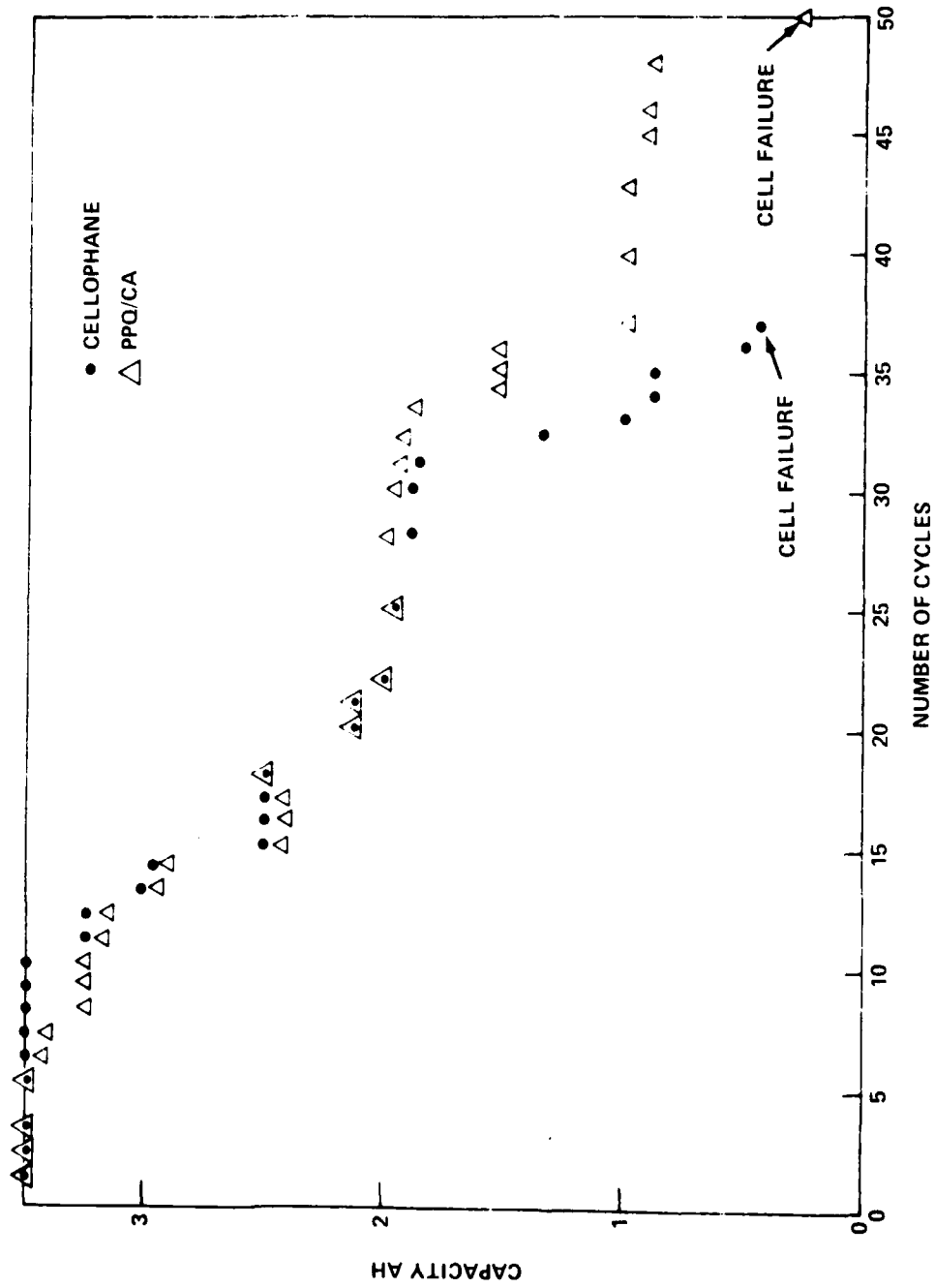


FIGURE 11 COMPARISON OF CYCLE LIFE CHARACTERISTICS OF PPQ/CA AND CELLOPHANE

CONCLUSION AND RECOMMENDATIONS

The new separator material PPQ/CA (60/40) is a good candidate for alkaline secondary battery applications. However, because of the high cost of the PPQ raw material the following recommendations are made:

a. Redirect our research efforts into other areas of separator technology i.e., nickel coated separators.

b. In the event that the Navy has a strong commitment to PPQ, one must spend large sums of money in developing inexpensive manufacturing technology of the polymer, as well as the blends and final membranes. One must remember that the samples produced in our laboratory are research samples and are not production line samples.

c. Since the cycle life improvement is not better than 25% over the state-of-the-art inexpensive materials, one should look into other high-technology areas for cost-competitive separators.

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